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PATENT SPECIFICATION

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(19)

(54) WATER-DISPERSIBLE PIGMENT COMPOSITIONS AND THEIR PRODUCTION

(71) We, HERCULES INCORPORATED, a Corporation organised under the laws of the State of Delaware, United States of America, of 910 Market Street, Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dry pigment compositions in water-dispersible form and more particularly to the production of dry pigment compositions which are easily dispersed in aqueous systems by hand mixing, which exhibit good flocculation resistance, and which develop upon dispersion in aqueous systems substantially the same strength and colour values as aqueous pigment dispersions.

In the past various methods have been proposed to overcome the difficulties of uniformly incorporating pigment in latex emulsion paints. For example, in U.S. Patent No. 3,067,053 to Tarantino there is described a method for coating pigment particles in presscake form with a non-ionic surface-active agent (with or without an anionic surface-active agent) to improve the ease of dispersion and produce colourants of outstanding strength and colour value. Slurries or pastes of these colourants are easily dispersed in latex system by a simple mixing or stirring operation and do not need to be milled to develop stable colour values. However, when such slurries or pastes are dried and powdered, ease of dispersibility, rate of colour development and strength are considerably reduced over their non-dried counterparts.

Tarantino in U.S. Patent No. 3,067,053 also suggests using certain thickeners in amounts from about 0.8 to about 6 per cent by weight of the dry pigment to control the viscosity of the pastes or slurries. Such thickeners are said to have no effect on the final tinctorial intensity of the pigment composition but, if a dry product is to be obtained, the thickener should be limited to pigmentary or cellulosic materials which are easily wettable, or dispersible after drying. The use of any colloid-type thickeners in an amount greater than 7 per cent is not taught by Tarantino.

Nagata et al. in U.S. No. 3,652,313 teach improving the dispersibility of pigments in latex paints by mixing the pigment with greater than 5 per cent and preferably from 10 to 30 per cent by weight of the pigment of a water-soluble hydroxyalkyl cellulose or a partially saponified poly(vinyl acetate) or its partially etherified derivative, and disclose that the pigment dispersions also show good redispersibility after drying. Nagata et al.'s dried dispersions, however, do not develop the full colour value or exhibit the flocculation resistance of their non-dried counterparts. Dry pigment compositions which are easily dispersed in aqueous systems and provide strength and colour qualities substantially equivalent to their aqueous counterparts are not produced according to the Nagata et al. patent.

In accordance with the invention described and claimed in our Application No. 2357/75 (Serial No. 1,489,693) we found that dry, water-dispersible compositions having broad compatibility in latex and other aqueous systems can be produced and that such dry compositions exhibit good flocculation resistance and develop substantially the same strength and colour value as aqueous pigment dispersions which have not been dried. The phrases "substantially the same as" and "substantially equivalent to", as used throughout this specification to denote strength and/or colour value of pigments, are intended to mean a strength or colour value which varies from the comparison by not more than about 5 per cent. Application No. 2357/75 (Serial No. 1,489,693) provides a process for preparing a dry water-dispersible pigment composition, and the compositions so produced, having the above properties, said process comprising the steps of: forming a homogeneous mixture comprising milled or homogenized pigment, water and, by weight of the pigment, (a) from 15 to 45 per cent

of a nonionic dispersing agent of the polyether alcohol type, the alkylene oxide-alkylene diamine block polymer type or the polyoxyethylene glycol or glycerol ester type, (b) from 10 to 70 per cent of at least one water-dispersible nonionic polymer selected from (1) an at least partially hydrolyzed polymer of vinyl acetate, (2) a polymer of an N-vinyl pyrrolidone and (3) mixtures thereof and (c) from 0 to about 40 per cent of a nonionic colloid; and removing the water from said mixture until a dry composition is obtained, the total amount of dispersing agent, polymer and colloid being from 20 to 45 per cent by weight of the dry composition and the weight ratio of polymer plus colloid to dispersing agent being greater than 0.85.

We have now found that the weight ratio of polymer plus colloid to dispersing agent need not be greater than 0.85. Accordingly the present invention provides a process and composition according to Application No. 2357/75 (Serial No. 1,489,693) modified in that said ratio is not greater than 0.85.

The compositions of the invention are thus dry pigment concentrates comprising from 55 to 80 per cent by weight of pigment and from 45 to 20 per cent by weight of a nonionic material comprising, based on the weight of the pigment, from 15 to 45 per cent of a nonionic dispersing agent of the polyether alcohol type, the alkylene oxide-alkylene diamine block polymer type or polyoxyethylene glycol ester or glycerol ester type, from 10 to 70 per cent of at least one water-dispersible nonionic polymer selected from (1) an at least partially hydrolyzed polymer of vinyl acetate and (2) a polymer of an N-vinyl pyrrolidone, and from 0 to 40 per cent of a nonionic colloid, the weight ratio of polymer plus colloid to dispersing agent being not greater than 0.85. Preferably the compositions are concentrates containing 60—75 per cent and most preferably 60—70 per cent pigment.

The invention can be practiced with the inorganic and organic prime pigments, extender pigments, metallic pigments, the various finely-divided channel and furnace blacks and the like. Typical pigments include organic pigments such as diarylide yellow, the phthalocyanine blues and green, the quinacridone reds and voilets, dioxazine violet and the like; and inorganic pigments such as the cadmium reds and yellows, the cadmium sulfide type pigments, the molybdate oranges, iron oxide yellow and red, and the like. Also suitable are the hydrophilic type pigments such as, for example, titanium dioxide and the lead chromate colours.

As stated above, the use of a certain type of non-ionic dispersing agent in an amount ranging from 15 to 45 per cent by weight of the pigment is necessary to the practice of this invention. The dispersing agents which have been found to be useful in this invention are of the types known as polyether alcohols, alkylene oxide-alkylene diamine block polymers and polyoxyethylene glycol esters or glycerol esters and generally have an HLB greater than 11 and preferably from 12 to 18. Preferred nonionic dispersing agents of the polyether alcohol type are the condensates of ethylene oxide and an alcohol such as a rosin alcohol or an alkyl phenol. Particularly preferred are the alkylaryl polyether alcohols which contain an average of 9 to 40 moles of ethylene oxide per mole of alcohol and contain alkyl groups of 8 or 9 carbon atoms. The polyether alcohol type dispersing agents are commercially available as the Tritons, (registered Trade Mark), e.g., X-100, X-102, N-101 and N-111 of Rohm and Haas Co., the Igepals of General Aniline & Film Corp., the Hyonics (registered Trade Mark) of Nopco Chemical Co. and the Tergitols (registered Trade Mark) of Union Carbide Corp. Typical of the alkylene oxide-amine block copolymer type dispersing agents are the materials formed to the addition of an alkylene oxide to an alkylene diamine, as for example by the addition of propylene oxide to ethylene diamine followed by the addition of ethylene oxide. Dispersing agents of this type are commercially available as the Tetronics of Wyandotte Chemicals Corp. Nonionic dispersing agents of the polyoxyethylene glycol or glycerol ester type include the ethoxylated fatty and rosin acid esters such as the polyoxyethylene glycol fatty and/or rosin acid esters and the polyoxyethylene fatty glycerides containing at least 10 moles of ethylene oxide per mole of such acids as coconut fatty acid, stearic acid, oleic acid and rosin/fatty acid combinations. Dispersing agents of this type are commercially available as the Ethofats (registered Trade Mark) of Armour Industrial Chemical Co. and Atlas G-1295 and G-1300 of Atlas Chemical Division of I.C.I. America, Inc. (Atlas is a registered Trade Mark).

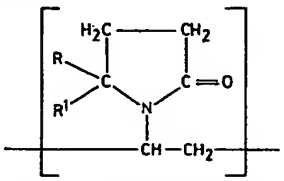
The amount of nonionic dispersing agent necessary will, as stated, fall within the range of 15 to 45 per cent by weight of the pigment and sufficient dispersing agent must be present to provide ease of processing and particle size reduction. Usually, an amount between 15 and 35 per cent by weight of the pigment will provide good dispersibility without detriment to any other desirable properties.

The practice of the invention also requires the presence of from 10 to 70 per cent by weight of the pigment of a water-dispersible nonionic polymer which is either an at least partially hydrolyzed polymer of vinyl acetate, a polymer of an N-vinyl pyrrolidone or a mixture thereof. The function of the polymer is multiphase since it acts synergistically with the dispersing agent to reduce the pigment

particle size beyond that which can be accomplished by the dispersing agent alone, acts as a coating for the pigment particles to prevent reagglomeration during the drying process, acts to prevent flocculation and provides broad compatibility in a broad variety of aqueous systems.

The at least partially hydrolyzed polymers of vinyl acetate which can be employed in the present invention are the completely water-dispersible and preferably the water-soluble products obtained by partial to complete hydrolysis of poly(vinyl acetate). While all molecular weights and degrees of hydrolysis are useful, the higher molecular weight grades disperse more slowly and the more highly hydrolyzed grades such as the fully hydrolyzed grades of poly(vinyl alcohol) reduce somewhat the water sensitivity of the pigment concentrates. The preferred hydrolyzed polymers of vinyl acetate which meet the above requirements and are useful in the practice of the invention include the water-soluble polymers which are at least 70 per cent hydrolyzed, and preferably 80 to 90 per cent hydrolyzed, and which have a molecular weight within the range of 2000 to 130,000, and preferably from 2000 to 95,000. Such polymers are available commercially as the Gelvatols (registered Trade Mark) (Monsanto Company), the Elvanols (E. I. du Pont de Nemours and Company), the Lemols (Borden Chemical Company) and the Vinols (Airco Corp.). Also useful are the water-soluble ether derivatives of the partially hydrolyzed poly(vinyl acetates) or the poly(vinyl alcohol)s wherein a portion and preferably at least 10 per cent of the hydroxyl groups are reacted with an alkylene oxide such as ethylene oxide.

The polymers of an N-vinyl pyrrolidone which are useful in the practice of the invention are the water-dispersible nonionic polymers. Particularly useful are polymers containing from 35 to 100 mole per cent of units of the formula:



wherein R and R′ are hydrogen, methyl or ethyl and from 0 to 65 mole per cent units of one or more monoethylenically unsaturated comonomers which will yield with the N-vinyl pyrrolidone nonionic copolymers having water-dispersibility. Thus the preferred N - vinyl pyrrolidones include N - vinyl pyrrolidone, N - vinyl - 5 - methyl pyrrolidone, N - vinyl - 5 - ether pyrrolidone, N - vinyl - 5,5 - dimethyl pyrrolidone, N - vinyl - 5,5 - diethyl pyrrolidone and N - vinyl - 5 - methyl - 5 - ether pyrrolidone.

Typical comonomers which can be polymerized with the N - vinyl pyrrolidones include vinyl esters such as vinyl acetate, acrylic acid esters such as ethyl acrylate, methacrylic acid esters such as methyl methacrylate, viny alkyl ethers such as vinyl cyclohexyl ether, vinyl halides such as vinyl chloride, allyl alcohol, acrylonitrile, vinyl carbazole and styrene.

The most preferred polymers of N - vinyl pyrrolidones are the homopolymers of N - vinyl pyrrolidone and its copolymers with vinyl esters having K-values from 10 to 140 and preferably from 10 to 60. Relative viscosity measurements which are designated as K-values are described in Modern Plastics, *23*, No. 3, pages 157—161, 212, 214, 216 and 218 (1945). The polymers are readily obtained by conventional polymerization procedures and are available commercially as the Plasdones, Polyclars and PVPs (General Aniline and Film Corp.).

Other nonionic materials can also be present providing they do not detract from the advantages of the invention, Particularly useful are the nonionic materials known as protective colloids. They can be present in amounts up to 40 per cent by weight of the pigment but usually will only be employed at low pigment concentrations. If present, the colloid will preferably comprise from 5 to 35 per cent and most preferably from 10 to 30 per cent by weight of the pigment. Useful colloids include the nonionic cellulose ethers, starches and starch derivatives, the natural gums, poly(alkylene oxides), poly(alkylene glycols) and polyacrylamide. Particularly preferred colloids are methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, starch pregelatinized starch, dextrin, hydroxypropyl starch, tapioca flour, wheat starch, casein, egg albumin, blood albumin, gelatin, bone glue, gum arabic, gum tragacanth, locust bean gum, polyacrylamide, and poly(ethylene oxide).

Other nonionic materials such as wetting agents, antifoaming agents, etc., can be included in amounts up to about 3 per cent by weight of the pigment, if desired.

As stated, the process of the invention comprises, in brief, the steps of forming a specific homogeneous mixture, and drying the mixture. The first step can be carried out in one or more stages. If one stage is used, all of the ingredients, i.e., the pigment, dispersing agent, polymer, colloid, if present, and water are milled or homogenized conventionally as, for example, in a pebble mill of a Gaulin homogenizer until a homogeneous mixture is formed. If two stages are employed, and such is generally preferred from the standpoint of economics, an aqueous dispersion of the pigment is first produced by milling or homogenizing the pigment in water in the presence of the nonionic dispersing agent, the pigment preferably being in press-

cake form and then the pigment dispersion so produced is intimately mixed in a second stage with the desired amount of the water-dispersible nonionic polymer and colloid, if employed. The mixing of the second stage can be carried out in any known manner for mixing solids and liquids and is suitably carried out by stirring and then homogenizing. The first step of the process is dehydration wherein the water is removed until a dry composition is obtained. Preferably the water is removed by spray drying which gives a finely-divided, dustless product directly. Alternatively, the water may be removed by tray drying and the dried product cryogenically ground to produce a product in powdery form.

The invention is further illustrated by the following examples wherein all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

198 parts of copper phthalocyanine green presscake containing 64.5 parts of pigment (dry basis), 16.15 parts of isooctyl phenyl polyethoxyethanol and 70 parts of water were added to a stainless steel tank equipped with an agitator and the tank contents were stirred for 30 minutes at 25°C until deflocculation had occurred. The deflocculated pigment was passed twice through a homogenizer, following the aqueous dispersion so produced was agitated for 30 minutes with 0.3 part of an anti-foaming agent, 12.9 parts of isooctyl phenyl polyethoxyethanol and 6.45 parts of the hydrolyzed poly(vinyl acetate) having an average molecular weight of 10,000 and residual poly(vinyl acetate) content of 19.5 to 21.5 per cent and being 87.7 to 89 per cent hydrolyzed. The mixture was passed twice through a homogenizer and the resulting homogenized mixture was air dried for 30 hours at 60°C. The dried product was mixed with dry ice in the weight ratio of about 10/1 and the mixture was micropulverized through a 1/16-inch screen. The resulting product was a dry redispersible concentrate containing 64.5 per cent pigment in the form of non-dusting particles.

The dispersibility characteristics of the pigmentary product of this Example were evaluated by hand mixing 1 part of the spray dried pigment concentrate with 100 parts of a commercial latex paint formulation (Regal Wall Satin) containing

per cent	
65.6	Titanium dioxide
20.1	Silicates
14.3	Film-forming vehicle (vinyl acrylic aqueous emulsion)

until a uniform paint dispersion was obtained (about 5 minutes). "Regal" is a registered Trade Mark. The paint dispersion was next separated into two equal portions and one portion was stirred for an additional 3 minutes using a propeller-type power stirrer. Visual comparison of the hand-mixed and the power stirred paints for tint strength on paper stock indicated no differences in tin strengths.

Tint strength and flocculation resistance of the hand-mixed and power-stirred paints were further evaluated by comparison with a control paint prepared in the same manner as above except that an equal mount on a pigment basis of an aqueous pigment dispersion was substituted for the spray-dried pigment concentrate.

When the product was evaluated in Regal Wall Satin according to the foregoing procedure, its colour strength, flocculation resistance and compatibility were substantially equivalent (at equal pigment level) to a control in which the aqueous pigment dispersion referred to was the aqueous counterpart of the pigment concentrate of this Example, i.e., the undried homogeneous mixture.

EXAMPLE 2

The procedure of Example 1 was repeated except that 6.45 parts of poly(N - vinyl pyrrolidone) having an average molecular weight of about 10,000 and a K-value of 15—21 were substituted for the hydrolyzed poly(vinyl acetate). The resulting product was a dry, redispersible concentrate containing 64.5 per cent pigment in the form of non-dusting particles. When the product was evaluated in Regal Wall Satin according to the procedure of Example 1, its colour strength, flocculation resistance and compatibility were substantially equivalent (at equal pigment level) to its aqueous counterpart and to the commercial aqueous pigment dispersion Super IMPerse Green (phthalocyanine)—X-3289—Hercules Incorporated.

WHAT WE CLAIM IS:—

1. A process for preparing a dry, water-dispersible pigment composition comprising the steps of: forming a homogeneous mixture comprising milled or homogenized pigment, water and, by weight of pigment: (a) from 15 to 45 per cent of a nonionic dispersing agent of the polyether alcohol type, the alkylene oxide-alkylene diamine block polymer type or the polyoxyethylene glycol ester or glycerol ester type; (b) from 10 to 70 per cent of at least one water-dispersible nonionic polymer which is (1) an at least partially hydrolyzed polymer of vinyl acetate, (2) a polymer of an N - vinyl pyrrolidone or (3) a mixture thereof; and (c) from 0 to 40 per cent of a nonionic colloid; and removing the water from said mixture until a dry composition is obtained, the total amount of dispersing agent, polymer and colloid being from 20 to 45 per cent by weight of the dry composition and the weight ratio of polymer

plus colloid to dispersing agent being not greater than 0.85.

2. A process according to Claim 1, comprising: (i) milling or homogenizing the pigment in water in the presence of component (a) to form an aqueous pigment dispersion; (ii) mixing said pigment dispersion with component (b) and component (c) until a homogeneous mixture is formed; and (iii) removing the water from said mixture.

3. A process according to Claim 1 or 2, wherein the water is removed from said mixture by spray drying the mixture.

4. A process according to any preceding Claim, wherein the polymer (b) is 80 to 90 percent hydrolyzed poly(vinyl acetate).

5. A process according to any of Claims 1 to 3, wherein the polymer (b) is poly(N-vinyl pyrrolidone).

6. A process for preparing a dry, water-dispersible pigment composition substantially as described in any of the foregoing Examples.

7. A dry, water-dispersible pigment composition comprising from 55 to 80 per cent of pigment and from 45 to 20 per cent of a nonionic material comprising, based on the weight of the pigment, from 15 to 45 per cent of a nonionic dispersing agent of the polyether alcohol type, alkylene oxide-alkylene diamine block polymer type or polyoxyethylene glycol or glycerol ester type, from 10 to 70 per cent of at least one water-dispersible nonionic polymer which is (1) an at least partially hydrolyzed polymer of vinyl acetate, (2) a polymer of N - vinyl pyrrolidone or (3) a mixture thereof; and from 0 to 40 per cent of a nonionic colloid, the weight ratio of polymer plus colloid to dispersing agent being not greater than 0.85.

8. A dry water-dispersible pigment composition produced according to any of Claims 1 to 6.

9. A composition according to Claim 7 or 8, wherein the colloid is a starch derivative which is present in an amount ranging from 5 to 35 per cent by weight of the pigment.

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